#### Form Approved REPORT DOCUMENTATION PAGE OMB NO. 0704-0188 Public Reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimates or any other aspect of this gathering and maintaining the data necess, and compressing and reviewing the contention of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188,) Washington, DC 20503. 1. AGENCY USE ONLY (Leave Blank) 2. REPORT DATE 3. REPORT TYPE AND DATES COVERED August 11, 1999 4. TITLE AND SUBTITLE 5. FUNDING NUMBERS Nanoscopic Studies of Quantum Effects in Silicon Quantum Dots DAAG55-97-1-0007 6. AUTHOR(S) Raphael Tsu 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) 8. PERFORMING ORGANIZATION UNC-Charlotte, Charlotte NC 28223 REPORT NUMBER 9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) 10. SPONSORING / MONITORING AGENCY REPORT NUMBER U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211 ARO 36223.1-EL 11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation. 12 a. DISTRIBUTION / AVAILABILITY STATEMENT 12 b. DISTRIBUTION CODE Approved for public release; distribution unlimited. 13. ABSTRACT (Maximum 200 words) Under ARO supports, we have advanced the following fundamental knowledge in

the man-made quantum phenomena: observation of resonant tunneling via the nanoparticles of silicon embedded in a silicon dioxide matrix; theoretical models of dielectric constant, doping, capacitance and excitons in Si nano-particle, and visible light emission from superlattices consisting of alternate layers of silicon with adsorbed oxygen forming an epitaxial Si/O superlattice. Moreover this superlattice represents a new kind under the name Semiconductor-Atomic-Superlattice (SAS). We have achieved several important breakthroughs: Si/O superlattice showing a 0.5eV barrier height; a nine-period system showing electroluminescence (EL) which has lasted for more than a year without degradation; and the continuation of silicon epitaxy beyond the adsorbed oxygen with low defect density arising from the monolayer of oxygen, being less than  $10^9\ / \text{cm}^2$ . The thin barrier is at most 1-2nm thick, which allows adjacent quantum states to couple strongly, forming an energy band.

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#### 1. BRIEF OUTLINE OF RESEARCH FINDINGS AND ACCOMPLISHMENTS

Under the ARO supports, we have advanced a number of fundamental understandings in the world of man-made quantum phenomena, these includes:

- Quantum confinements in nanoscale silicon particles embedded in an oxide matrix and the
  observation of resonant tunneling via the nano-particles. The silicon nano-particles
  embedded in an amorphous oxide matrix were produced by annealing and/or oxidation of a
  thin (10-20nm) a-Si. Transport through this layer established tunneling through quantum
  states of the nano-particles.
- Theoretic models of dielectric constant, doping, capacitance and excitons in Si nanoparticles.
- Visible Light emission in Si nanoparticles, both in Porous Si and in an oxide matrix.
- Epitaxial barrier in silicon: with multi layers of Si/adsorbed oxygen. Silicon epitaxy beyond the disordered monolayer of adsorbed oxygen has low defect density, being less than 10° /cm². This Si/O superlattice barrier forms the basis of silicon quantum devices. A 2-period structure shows an effective barrier height of 0.5eV, sufficient for most silicon quantum devices at room temperature. The structure may be used to replace silicon on insulator (SOI) for high speed, low power transistors of the future.
- An electroluminescent diode structure consisting of a 9 period of Si (1.1nm) / monolayer of adsorbed oxygen superlattice shows visible light with a peak at 2.2eV life-tested for more than one year without degradation.
- The time for thinking of an all silicon optoelectronic device is at hand-an electronic and photonic superchip.

### 4. Statement of the problem studied

Quantum mechanical devices utilize the wave nature of electrons for their operations whenever the electron mean-free-path exceeds the appropriate dimensions of the device structure. In the past several years, certain schemes appeared which may facilitate the realization of silicon quantum devices, such as the resonant tunneling via nanoscale silicon particles imbedded in an oxide matrix, and the superlattice barrier for silicon consisting of several period of Si/O. Our main finding for the observation of tunneling via quantum states represented by silicon nano-particles embedded in an oxide matrix is the use of a controlled forming process.

Epitaxially grown silicon beyond the superlattice barrier region, consisting of adsorbed oxygen is low in stacking fault defects, and thus is potentially important for silicon based quantum devices, including electroluminescent diodes, as well as serving as an SOI ( silicon on

insulator). The replacement of SOI by the epitaxially grown Si/O superlattice barrier should promote the effort in high speed and low power MOSFET devices.

# 5. Summary (also see 1.)

Speed and density go together: scaling down the device size leads to higher speed and density. How far can scaling go? Operating voltages are set by the thermal voltage. Reducing size results ultimately to highfields beyond the breakdown. Besides, quantum effects will be reached at some point. These effects are not all desirable, for example, quantum interference is too size dependent, demanding unrealistic manufacturing tolerances. As the size approaches few nm, it is even impossible to dope due to the drastic increase in the binding energy of dopants. Classically, one talks about storing charges, as we have seen that quantum mechanically, one can only confine charges with a barrier. And electrons and holes confined in a barrier do leak out. Surely one can use thicker barrier to reduce tunneling, then, it is not possible to quickly remove the confined particle unless a large barrier lowering field is applied. The problem with this scheme is that one needs to localize the applied field, otherwise many adjacent structures will be affected. What is needed is judicious applications of quantum effects far from the notion that quantum transistors must be better! Fortunately, what is focussed in this report is not about wide spread utilization of quantum confinement. Rather, in some specific applications, for example,(a) the epitaxial Si/O superlattice for replacing the SOI fabricated by ion-implantation, (b) fabrication of a RTD in silicon, (c) increasing the oscillator strength of silicon by quantum confinement for optoelectronic purposes, and (d) discretizing the I-V as resonant tunneling via nanoscale particles for multistage logic and functional devices. After stating all that, I am impelled to be optimistic that a totally new system fully utilizing the wave nature of quantum mechanics is right around the corner, waiting to be explored, even in silicon. The task at hand is huge, therefore, it is important to sort out those goals which can be successfully pursued with the available funding, to arrive at some consensus among the researchers for future endeavors.

Although much of this report has been summarized in the publication, Room Temperature Silicon Quantum Devices, R. Tsu, in International J. High Speed Electronics and Systems, editors M. Dutta and M. Stroscio, 9, (1), 145 (1998); I like to include three figures:

Fig.1 showing the high resolution TEM of the epitaxy beyond the O/Si/O/Si/O (whitish region),

Fig.2 showing a plane view-TEM Si/O with  $10^8 - 10^9$  /cm<sup>2</sup> defect density, and

Fig.3 showing the electroluminescence of a 9-period Si(1.1nm)/O superlattice under the application of 10V reverse bias operating continuously for over one year.

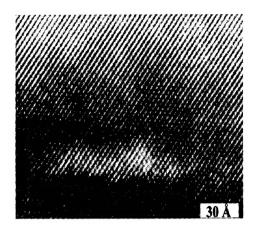


Fig.1 High Resolution showing the continuation of epitaxy beyond the O/Si/O/Si/O (white region)

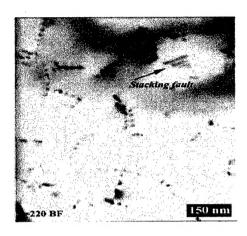


Fig.2 Plane View – TEM: Si/O (2.5nm) showing 10<sup>9</sup>/ cm<sup>2</sup> defect density



Fig.3 Electroluminescence of a 9-period Si/O – superlattice. The green emission shows the active EL from  $0.5 \times 1.2$ mm thin partially transparent gold contact

It is commonly assumed that the Si/Ge superlattice system is the only quantum devices possible. I like to point out that the Si/Ge system restricts quantum confinement in the Ge. Therefore the Si/Ge system is a Ge system rather than a Si system! All the results reported here involve quantum confinement in silicon, therefore, silicon quantum devices are potentially possible with the Si/O superlattice system.

In conclusion, quantum devices involving silicon nanoparticles cannot be implemented yet because size control, which calls for much larger effort, has not been perfected. On the other hand, the Si epitaxy sandwiched between adsorbed species is demonstrated, which is ready for playing an important role in quantum devices, particularly, the optoelectronic devices.

#### 6. Publications

# The publication list important to this proposed study:

- 107. Optical Properties of Quantum Steps, H. Shen, F. H. Pollak and R. Tsu, Appl. Phys. Lett. 57, 13 (1990).
- 108. Some New Insights in the Physics of Quantum Well Devices, R. Tsu, SPIE 1361, 231 (1990).
- 109. Resonant Tunneling in Microcrystalline Si Quantum Box Diode, R. Tsu, Q. Y. Ye and E. H. Nicollian, SPIE <u>1361</u>, 313 (1990).
- 112. Resonant Tunneling Via Microcrystalline Silicon Quantum Confinement, Q. Y. Ye, R. Tsu and E. H. Nicollian, Phys. Rev. B <u>44</u>, 1806 (1991).
- 114. Correlation of Raman and Photoluminescence Spectra of Porous Silcon, R. Tsu, H. Shen and M. Dutta, Appl. Phys. Lett. <u>60</u>, 112 (1992).
- 115. Microstructure of Visible Luminescent Porous Silicon, M. W. Cole, J. F. Harvey, R. A. Lux, D. W. Eckart and R. Tsu, Appl. Phys. Lett. <u>60</u>, 2800 (1992).
- 122. Transport in Nanoscale Silicon Clusters, R. Tsu, Physica B 189 235 (1993).
- 124. Electrical Properties of a Silicon Quantum Dot Diode, E. H. Nicollian and R. Tsu, J. Appl. Phys. 74, 4020 (1993).
- 125. Silicon Quantum Well with Strain-Layer Barrier, R. Tsu, Nature 364, 19 (1993).
- Physics of Extreme Quantum Confinement Exemplified by Si/SiO2 System, R. Tsu, in The Physics and Chemistry of SiO2 and the Si-SiO2 Interface 2, Eds. C.R.Helms and B.E. Deal (Plenum Press, Pub. 1993) p.353
- 131. Doping of a Quantum Dot, R. Tsu and D. Babic, Appl. Phys. Lett. 64, 1806 (1994).
- 133. Slow Conductance Oscillations in Nanoscale Clusters of Quantum Dots, R. Tsu, X. L. Li, and E. H. Nicollian, Appl. Phys. Lett. <u>65</u>, 842 (1994).
- 140. Visible Light Emission in Silicon-Interface Adsorbed Gas Superlattices, R. Tsu, J. Morais, and A. Bowhill, Mat. Res. Soc. Symp. Proc. 358, 825 (1995).
- 141. Avalanche Amplification of Resonant Tunneling through Parallel Silicon Microcrystallites, Phys. Rev. <u>B51</u>, 13337,(1995)
- 144. Correlation of Raman and Optical studies with AFM in Porous Si, Adam A. Flilios, Susan

- S. Hefner, and Raphael Tsu, J. Vac. Sci. & Tech. B14,3431(1996)
- A Simple Model For The Dielectric Constant Of Nanoscale Silicon Particle, R.
   Tsu, D.Babic, and L.Ioriatti, J. Appl. Phys. <u>82</u>, 1327(1997)
- 145. Exciton in Nanoscale Silicon Quantum Dots, D.Babic and R. Tsu, Superlattice and Microstructure, 22, 581(1997)
- The Determination of Activation Energy in Quantum Wells, J. Ding and R. Tsu, Appl. Phys. Lett. <u>71</u>, 2124 (1998)
- 148 Visible Electroluminescence in Si/absorbed Gas Superlattice, R. Tsu, Q.Zhang, and A.Filios, SPIE <u>3290</u>, 246, (1998).
- 151 Silicon Epitaxy on Si(100) with Adsorbed Oxygen", R. Tsu, A.Filios, C.Lofgren, K.Dovidenko, and C.G.Wang, Electrochem. & Solid State Lett. 1, 80(1998).
- Photovoltaic Effects", D. Boeringer and R. Tsu, in Encyclopedia of Electrical and Electronic Engineering, ed. J.G. Wester (John Wiley & Sons, NY 1998).
- Room Temperature Silicon Quantum Devices, R. Tsu, in International J. High Speed Electronics And Systems, editors M. Dutta and M. Stroscio, 9, (1), 145 (1998)
- 155 Perspectives of Light Emitters in Nanoscale Silicon, R. Tsu, 9<sup>th</sup> Cimtec-World Forum on New Materials, Symp.X-Innovative Light Emitting Materials, P. Vincenzini, G.C.Righini (Editor) Techna Srl,1999
- 7. List of Participants (Including those supported by previous ARO grant, also some of those listed were supported for only part of the grant period)

### Postdoctoral fellows

Dr. Q. Zhang

Post-doctoral fellow, Jan. 1998 - Dec. 1998 (1/4)

Dr. Jinli Ding

Post-doctoral fellow, Jan. 1998 - Mar. 1998(1/4), now at U. Toronto

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A. Filios

Ph.D., May 1999 (1/4), MS 1995

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MS Fall 1998 (1/2)

F. de Freitas

MS candidate, April 1998 – Dec. 1998 (1/4)

C. Lofgren

MS 1993, Ph.D. Candidate Joint NC-State/UNCC program

# 8. Reports of Inventions:

No Invention was disclosed under this contract on Proposal No. 36223-EL, DAAG55-97-1-0007, entitled: Nanoscopic Studies of Quantum Effects in Silicon Quantum Dots. However, prior to the funding of this proposed studies became finalized, this investigator was associated with the ETDL of the US Army Communications-Electronics Command, Fort Monmouth NJ 07703, via a GEO Contract DAAL01-89-C-0927, where he was involved with others on the following disclosures closely related to the proposed work.

- Patent filed 8/13/97, #08/915,547, Negative Differential Resistance Device Based on Tunneling Through Microclusters, and Therefor, AMSEL-LG-L Fortmonmouth, NJ 07703-5000, by James F. Harvey, Robert A. Lux and Raphael Tsu. This disclosure deals with tunneling through resonant energy levels in microclusters to acieve NRD, and hence oscillator, amplifier, and mixer, devices, based on the crystallization and oxidation of silicon clusters forming Si particles embedded in an amorphous silicon dioxide matrix between contacts. This is precisely the research topic of this proposed studies.
- Patent issued, May 6, 1997, #5,627,386, Silicon Nanostructure Light-Emitting Diode, by James F. Harvey, Robert A. Lux and Raphael Tsu, with assignee: The United States of America as represented by the Secretary of the Army. This patent deals with means to fabricate nanometer silicon tips to breakdown the momentum conservation resulting in light emission, which is closely related to the electroluminescence devices reported in the interim report dated April 8, 1999.

Both were filed by Fort Monmouth, Administered by Judith E. Cleveland, paralegal Specialist.